

The University of Chicago

ABSORPTION AND FLUORESCENCE
SPECTRA OF THE BIVALENT
EUROPIUM ION

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
MARCH, 1944

By
SEYMOUR KATCOFF

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This investigation would have been impossible without the generous assistance and co-operation of several people. First I wish to express my gratitude to Professor Simon Freed, who first suggested that the spectrum of bivalent europium should be investigated and who offered many valuable suggestions during the progress of the research. Dr. William Robinson has given valuable advice on crystal growing technique at high temperatures. The platinum wound resistance furnace which was used for making mixed alkaline earth fluoride crystals was borrowed from the Department of Geology through the generosity of its Chairman, Professor Edson S. Bastin.

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Finally I wish to express my gratitude to Mr. Leonard Treiman and Dr. Nathan Sugarman, whose help and advice were always available.

INTRODUCTION

The absorption and fluorescence spectra of the trivalent europium ion have been investigated in some detail but the spectra of bivalent europium have received little attention. Karl Przibram¹ and a few other investigators have observed a broad blue fluorescence band in certain naturally occurring fluorites which Przibram proved was caused by the presence of bivalent europium. He also prepared some pure EuCl_2 which showed the same blue fluorescence at room temperature and at -180°C . Herbert N. McCoy² observed that a 20-30% aqueous solution of europous chloride had a greenish yellow color, that all visible light was absorbed below about 4480Å, and that in the visible range of the spectrum no discrete bands were present. At the suggestion of Professor Freed, H. J. Steinberger investigated the ultraviolet absorption of dilute aqueous solutions of europous chloride with the hope of finding some discrete lines or bands.³ These were looked for because the Eu^{++} ion is isoelectronic with the Gd^{+++} ion which is known to have several groups of absorption lines and a group of fluorescence lines, all lying in the ultraviolet. The europous chloride solutions, however, showed a very intense continuous absorption which began at about 4100Å and extended throughout the ultraviolet. With a very dilute aqueous solution a weak diffuse band showing some signs of finer structure was observed at about 3200Å superimposed upon the continuum. In order to help establish the nature of the spectrum it was decided to examine the spectra of the ion in crystals where the electric fields are more symmetrical than in solution. Furthermore, the temperature could be greatly reduced to minimize the complications arising from thermal motion. When investigating the absorption spectrum of the Eu^{++} ion in crystals it is desirable to use a solid solution of the europous salt in another salt with the same anion

¹Karl Przibram, Zeit. für Physik, 107, 709 (1937).

²H. N. McCoy, J. Amer. Chem. Soc., 58, 1580 (1936).

³Private Communication.

which is transparent in the visible and ultraviolet. In this way the europous salt can be diluted to the extent necessary for allowing some light to penetrate the very intense ultraviolet continuum. Strontium (Sr^{++}) was chosen as the most suitable cation because its ionic radius, 1.13Å, is very close to that of Eu^{++} , 1.17Å.⁴ Steinberger found that crystals of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ containing about 1% Eu^{++} showed a group of absorption lines at 3200Å superimposed upon the usual strong continuous absorption. No resemblance to the structure of the Gd^{+++} spectrum could be recognized.

The present series of experiments was concerned with the investigation of the absorption and fluorescence spectra of the Eu^{++} ion in several kinds of mixed crystals: anhydrous EuCl_2 in SrCl_2 , anhydrous EuCl_2 in SrCl_2 with 5% BaCl_2 , anhydrous EuCl_2 in SrCl_2 with 10% BaCl_2 , $\text{Eu}(\text{NO}_3)_2$ in $\text{Sr}(\text{NO}_3)_2$, and EuF_2 in each of the alkaline earth fluorides (CaF_2 , SrF_2 , and BaF_2). The spectrum of Eu^{++} in $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ crystals was also investigated further. The spectra of the mixed fluoride crystals were complicated by the fact that most of the Eu^{++} had been oxidized to the trivalent state during the preparation of the crystals. The spectrum of trivalent europium, Eu^{+++} , was therefore mixed with that of Eu^{++} for these fluoride crystals. Detailed results are given below.

⁴Linus Pauling, J. Amer. Chem. Soc., 59, 1132 (1937).

EXPERIMENTAL

Preparation and Analyses of Crystals

Crystals grown from aqueous solution.--In order to prepare mixed crystals of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ in which some of the strontium was replaced by bivalent europium a saturated solution of strontium chloride was first prepared which was about 2N. in HCl and which contained a small amount of europic chloride. Three small beakers were placed in a desiccator charged with a few grams of calcium chloride. The air in the desiccator was displaced with nitrogen and the solution was then slowly passed through a short column of zinc for the purpose of reducing the europium to the bivalent state. The narrow exit tube at the bottom of the zinc column passed into the desiccator so that the solution could be distributed among the three beakers within. A tiny seed crystal of pure $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ was added to each of the three beakers and a very slow stream of nitrogen was maintained through the desiccator. Frequently the original seed crystal would slowly dissolve because the solution was slightly undersaturated. Then another seed would be added. When the solution reached saturation and the water continued to evaporate slowly, either the seed crystal would grow or a great many new tiny crystals would separate out. In the latter case a drop of water would be added to dissolve the crystals. The solution was then warmed by irradiation with an infra-red lamp to destroy all microscopic seed crystals that might still be present. After the solution had cooled to room temperature again, another seed crystal was added. After a few trials extending over a period of two or three days crystals several millimeters long and a few millimeters wide were usually obtained. These were trigonal crystals of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ in which 1% or less of the Sr^{++} ions were replaced by Eu^{++} ions.

Special precautions were necessary in growing mixed anhydrous crystals of $\text{Eu}(\text{NO}_3)_2$ in $\text{Sr}(\text{NO}_3)_2$ from aqueous solution. One difficulty arises from the fact that the Eu^{++} ion, which is a powerful reducing agent, is rapidly oxidized by nitric acid.

Furthermore, strontium nitrate crystallizes from water as cubic anhydrous crystals only at temperatures above 29.3°C . Oxidation of the europous ion was prevented by the following method. A few milliliters of an aqueous solution of europic and strontium nitrates containing only a trace of nitric acid was passed through a column of granulated zinc. This reduced the europium to the bivalent state. The solution then passed directly into a larger volume of a solution of strontium nitrate at about 90°C . which contained a few suspended particles of SrCO_3 . These immediately neutralized any trace of nitric acid which may have come through with the europous nitrate. An atmosphere of carbon dioxide was maintained over the solution to prevent oxidation by the air. The concentrations were adjusted so that the final solution was somewhat less than saturated with respect to $\text{Sr}(\text{NO}_3)_2$ at 90°C . and so that the amount of $\text{Eu}(\text{NO}_3)_2$ was about one mole per cent of the $\text{Sr}(\text{NO}_3)_2$. The vessel containing the solution was put into an oven at 90°C . and the temperature was then lowered slowly, over a period of several hours, to 40°C . Relatively large mixed crystals (2-3 mm. in diameter) crystallized out in this way. Chemical analysis of the crystals by titration with standard iodine solution showed that the europium was all present in the bivalent form.

Crystals grown from the fused salts.--All of the anhydrous chloride crystals were grown from the fused salts. A special glass apparatus (Fig. 1) was constructed to prepare the mixed salt in powdered form first. The air in the apparatus was completely displaced by carbon dioxide. Cap E was removed temporarily to introduce several milliliters of concentrated hydrochloric acid into tube F through the side-arm. A very slight excess of CO_2 pressure was applied in the flask below to prevent the acid from leaking through the selas (porous clay) disc. A solution 2N. in HCl containing a small amount of europic chloride and saturated with strontium chloride was added near the top at ground glass joint B. CO_2 pressure was applied through stopcock A, stopcock C was opened, and the solution was forced through the zinc column. This reduced the europium to the bivalent state. The solution then passed directly into tube F where the concentrated HCl causes the strontium chloride and europous chloride to precipitate together as mixed crystals. Stopcock C was then closed, the slight excess pressure was released from the flask, and pressure was maintained through stopcock A. This filtered off the supernatant

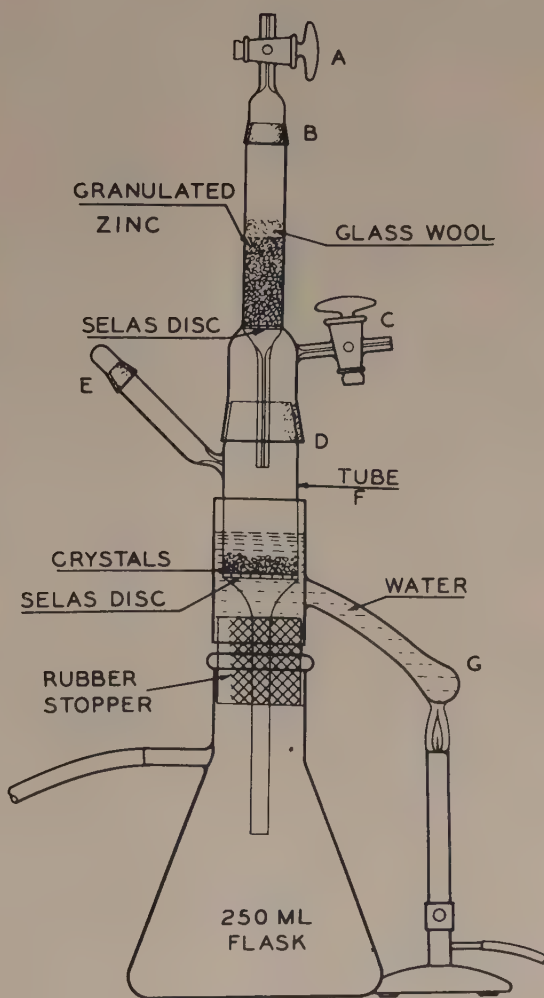


FIGURE 1

liquid from the crystals. They were washed with concentrated HCl which was again introduced through E. The powdered crystals which collected on the selas disc at the bottom of tube F were dried as follows. Carbon dioxide was passed over the crystals which were heated to about 100°C . by boiling water in the jacket surrounding tube F. After about forty minutes the powder was anhydrous and dry. In this form oxidation of the europous chloride by the air is very slow. Therefore ground glass joint D was opened and the crystals transferred to a porcelain or platinum crucible. This was covered and quickly placed at the bottom (closed end) of a quartz or sillimanite tube which was then attached by means of a ground joint to a vacuum line. The tube was evacuated and its temperature was raised slowly by means of an electric resistance furnace to about 600°C . over a period of two hours. Then the temperature was raised rather quickly to about 1000°C . where it was allowed to remain for thirty minutes. This insured complete melting of the crystals (m.p. of pure SrCl_2 is 873°C .). The temperature was lowered to about 830°C . and kept constant there for about two hours to allow the mixed salt to crystallize out. Then the crystals were slowly cooled to room temperature. A titration with standard iodine solution showed that the europium was in the bivalent form.

Mixed crystals of CaF_2 , SrF_2 , or BaF_2 with 1% europium fluoride were prepared in a similar manner. A solution containing alkaline earth chloride and europic chloride were passed through the zinc column and into a solution of ammonium fluoride (in tube F, Fig. 1). This precipitated the mixed fluoride which was then washed with water and dried as described above. It was transferred to a platinum crucible which was then placed in the sillimanite tube. It was heated in vacuum by means of a platinum wound resistance furnace to about 1000°C . and then an atmosphere of helium was passed in to minimize the danger of vaporization of the salt as the temperature was raised still higher. The maximum temperature was about a hundred degrees above the melting point of the particular fluoride used. In the case of SrF_2 this maximum was 1650°C . The temperature was later lowered to about $50^{\circ}\text{--}70^{\circ}$ below the melting point where it was kept for two to three hours as before. Then the temperature was lowered slowly to room temperature. These crystals were always translucent, never transparent. Even the fluorides which were prepared without any

europium (to serve as blanks) were translucent. Chemical analysis of the mixed fluoride crystals showed that 90% or more of the europium was in the trivalent form. Obviously most of the europous fluoride had been oxidized during the preparation of the crystals. H. N. McCoy has observed that pure europous fluoride oxidizes rapidly in air.⁵ The helium used may have been contaminated with oxygen.

Spectrographic Apparatus and Technique

Each crystal was mounted in a hole cut in the center of a piece of cork. All crevices between the crystal and the cork were covered with black paper to prevent any light from leaking around the crystal. This was then sandwiched between two thin plates of quartz which were held together by adhesive tape. The crystal was thus partially protected from the air. A small quartz dewar (partly unsilvered) containing liquid nitrogen or hydrogen was used to maintain the crystal at the desired low temperature. The level of the liquid nitrogen was always maintained just below the crystal in order to avoid the absorption bands from oxygen which is usually present as an impurity in the liquid nitrogen. Good thermal contact was maintained by means of two thick copper plates with a hole in each for allowing the light to pass.

A 200 watt tungsten projection lamp was used as light source for photographing the absorption spectra in the range between 3400Å and 8500Å. For spectra below 3400Å a hydrogen discharge tube was employed. A quartz lens after the light source focused the maximum amount of light upon the crystal. Then a second lens beyond the crystal focused the transmitted light upon the slit of a spectrograph. This was a quartz Hilger E-1 Littrow spectrograph which has a dispersion of 17Å per mm. at 4500Å and 37Å per mm. at 6000Å. Fluorescence spectra were excited by means of near ultraviolet light obtained from a small Bausch and Lomb carbon arc. The visible light was filtered out with a solution of copper sulfate and a Corning glass filter (No. 548, 587, or 986). Exposure times varied from a few minutes to several hours. The iron spectrum served as a reference for measuring the positions of the lines and bands.

⁵H. N. McCoy, J. Amer. Chem. Soc., 61, 2456 (1939).

RESULTS

Only one aspect of the spectrum of bivalent europium is common to all of its salts and solutions. That is a very intense continuous absorption which extends throughout the ultraviolet region up to about 4000-4500Å in the violet. In certain mixed crystals containing about one-tenth to one mole per cent Eu^{++} ions, absorption lines and bands are superimposed upon this continuum. Some kinds of crystals show diffuse fluorescence bands. Others show, in addition, sharp fluorescence lines at low temperatures.

When the spectrum of a crystal of anhydrous strontium chloride containing about one-tenth mole per cent of EuCl_2 was examined at room temperature, an intense absorption band (100Å wide) was found at 3270Å and a much weaker one was found at 3450Å (Table 1). At 85°K. a few more weak broad maxima appeared, but in addition a series of about fifty absorption lines was super-

TABLE 1
DIFFUSE ABSORPTION OF EuCl_2 IN SrCl_2 CRYSTALS

85°K.				195°K.				300°K.			
λ	ν	Width	Int.	λ	ν	Width	Int.	λ	ν	Width	Int.
3912Å	25,555	80Å	3	3890Å	25,700	100Å					
3780	26,446	50	2								
3600	27,770	140	3								
3480	28,727	70	4	*				3450Å	28,977	70Å	1
3288	30,404	90	10	*				3270	30,572	100	10
3066	32,605	50	2	*							

*At 195°K. the spectrum was not investigated below 3500Å.

imposed upon the diffuse bands (Table 2 and Fig. 2). These lines extended from 4000Å to 3300Å. Thirteen more lines were found between 3070Å and 2900Å. A large number of the lines were rather equally spaced, the intervals amounting to about 100-110 cm^{-1}



Fig. 2.--Absorption of $\text{EuCl}_2\text{-SrCl}_2$ crystals at (a) 300°K ., (b) and (c) 85°K ., and (d) 20°K . The emission lines superimposed upon (a) and (b) are from the hydrogen discharge which was used as source.

TABLE 2
LINE ABSORPTION OF $\text{EuCl}_2\text{-SrCl}_2$ CRYSTALS

85°K.			20°K.		
λ	ν	Int.	λ	ν	Int.
3991.2A	25,047 cm^{-1}	10	3993.5A	25,033 cm^{-1}	8
3971.5	25,172	3	3975.2	25,149	3
3957.8	25,259	8	3959.6	25,248	10
3940.4	25,371	6	3941.7	25,362	9
3928.1	25,450	0			
3925.5	25,467	6	3926.5	25,461	8
3908.2	25,580	6	3908.7	25,577	8
3892.6	25,682	4	3892.9	25,680	4
3877.4	25,783	0			
3875.2	25,797	3	3876.6	25,788	4
3860.4	25,897	1	3860.4	25,896	2
3843.5	26,010	9	3845.1	26,000	10
3826.2	26,128	4	3827.1	26,122	6
3819.2	26,176	2	3820.7	26,166	3
3812.8	26,220	7	3814.0	26,212	7
3795.6	26,338	4	3796.5	26,332	6
			3789.5	26,381	2
3782.0	26,433	4	3783.3	26,424	4
3765.1	26,552	3	3765.8	26,547	4
3749.2	26,664	2	3752.2	26,643	1
3737.4	26,748	10	3738.8	26,738	10
3721.4	26,864	3	3722.6	26,855	4
3707.7	26,963	10	3709.6	26,949	10
3692.4	27,074	4	3694.0	27,063	4
3678.5	27,177	6	3679.9	27,167	8
3665.8	27,271	5	3667.6	27,258	7
3651.3	27,380	5	3651.9	27,375	7
3645.0	27,427	0			
3637.6	27,483	4	3639.3	27,470	7
3623.4	27,590	4	3624.6	27,582	6
3617.1	27,638	4	3618.6	27,628	7
3608.8	27,702	3	3611.1	27,685	5
3594.9	27,809	2			
3589.4	27,851	3	3591.5	27,836	5
3561.6	28,069	2			
3549.1	28,168	4	3550.4	28,158	9
3530.8	28,314	5	3532.5	28,300	9
3522.7	28,379	3	3522.9	28,377	7
3516.7	28,427	3	3518.2	28,415	7
3505.1	28,522	4	*		
3490.3	28,642	3			
3477.9	28,744	3			
3466.2	28,842	3			
3422.2	29,212	3			
3367.1	29,690	2			
3336.9	29,959	5			
3333.5	29,989	9			
3327.9	30,040	2			
3320.9	30,103	1			

TABLE 2 - Continued

85°K.			20°K.		
λ	ν	Int.	λ	ν	Int.
3313.1A	30,174cm ⁻¹	3			
3309.9	30,203	5			
3065.0	32,618	1			
3058.6	32,686	1			
3038.6	32,901	3			
3018.5	33,120	3			
3008.5	33,230	2			
3000.5	33,319	2			
2975.2	33,602	4			
2966.2	33,704	3			
2957.1	33,808	4			
2947.7	33,915	2			
2938.5	34,022	2			
2928.9	34,133	2			
2920	34,237	0			

*At 20°K. no data were obtained beyond this point.

(Table 3). At 20°K. the absorption lines were much sharper and shifted slightly toward the red; the diffuse absorption bands were much weaker in relation to the lines. Some mixed crystals were prepared in which part of the SrCl₂ was replaced by BaCl₂ and in which the EuCl₂ content remained 0.1% as before. Two such batches were made. One contained 5% BaCl₂, the other 10% BaCl₂. All the crystals had the same cubic fluorite crystal structure. The added BaCl₂ only increased the lattice constant slightly. At 85°K. these crystals did not show the series of absorption lines but at 20°K. the lines did appear (Table 4). They were weak, somewhat wider, and shifted slightly toward shorter wave lengths (about 44cm⁻¹ for the 5% BaCl₂ crystals and about 85cm⁻¹ for the 10% BaCl₂ crystals). The diffuse absorption bands were unchanged also except for the same shift toward shorter wave lengths. A few additional weak lines appeared at longer wave lengths than that of the first line of the EuCl₂-SrCl₂ crystals (3993.5A).

An intense violet-blue fluorescence band (maximum at 4060A) and one in the extreme red at 7000A were found for the EuCl₂-SrCl₂ crystals at room temperature. However at the temperature of liquid nitrogen sharp fluorescence lines were found superimposed upon the violet-blue band and many lines appeared in the

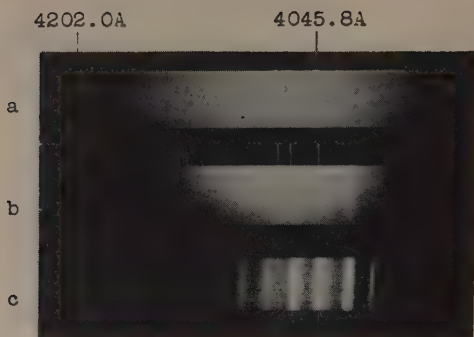


Fig. 3.--Violet fluorescence of $\text{EuCl}_2\text{-SrCl}_2$ crystals at (a) 300°K., (b) 85°K., and (c) 20°K.

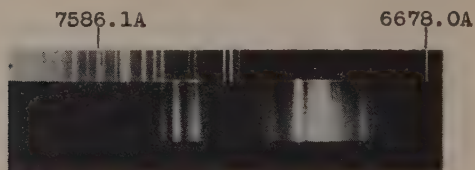


Fig. 4.--Red and infra-red fluorescence of $\text{EuCl}_2\text{-SrCl}_2$ crystals at 85°K.

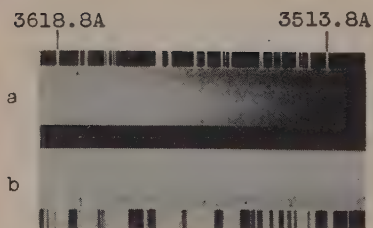


Fig. 5.--Absorption of Eu^{++} in $\text{SrCl}_2\cdot 6\text{H}_2\text{O}$ at (a) 300°K. and (b) 85°K.; light parallel to optic axis.

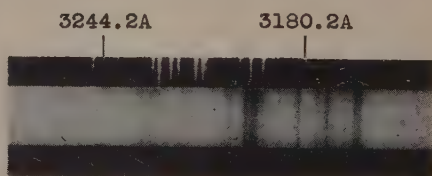


Fig. 6.--Absorption of Eu^{++} in $\text{SrCl}_2\cdot 6\text{H}_2\text{O}$ at 85°K.; light perpendicular to optic axis.

TABLE 3

OBSERVED ENERGY INTERVALS IN ABSORPTION SPECTRUM
OF $\text{EuCl}_2\text{-SrCl}_2$ CRYSTALS AT 85°K .

	$\Delta \nu$		$\Delta \nu$
25,172-25,047 cm^{-1}	125 cm^{-1}	27,483-27,380 cm^{-1}	103 cm^{-1}
25,259-25,172	87	27,590-27,483	107
25,371-25,259	112	27,702-27,590	112
25,467-25,371	96	27,809-27,702	107
25,580-25,467	113	28,168-28,069	99
25,682-25,580	102	28,427-28,314	113
25,797-25,682	115	28,522-28,427	95
25,897-25,797	100	28,642-28,522	120
26,128-26,010	118	28,744-28,642	102
26,220-26,128	92	28,842-28,744	98
26,338-26,220	118	30,103-29,989	114
26,433-26,338	95	30,203-30,103	100
26,552-26,433	119	33,120-32,901	119
26,664-26,552	112	33,230-33,120	110
26,864-26,748	116	33,704-33,602	102
26,963-26,864	99	33,808-33,704	104
27,074-26,963	111	33,915-33,808	107
27,177-27,074	103	34,022-33,915	107
27,271-27,177	94	34,133-34,022	111
27,380-27,271	109	34,237-34,133	104

extreme red and near infra-red (Tables 5 and 6, Figs. 3 and 4). The last violet fluorescence line toward the ultraviolet (3991A) coincides with the first absorption line. The spacing between most of the violet-blue lines is also $100\text{-}110\text{cm}^{-1}$. A few additional fluorescence lines were found at 3150A.

Hydrated strontium chloride crystals, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, in which about one mole per cent of the Sr^{++} ions are replaced by Eu^{++} ions, display a different spectrum. There is a continuous absorption in the ultraviolet but there are no superimposed diffuse absorption bands and no fluorescence at all. When light is passed through 6 mm. of a crystal (trigonal system) perpendicular to its optic axis, a group of about twenty absorption lines are obtained near 3200A (Table 7, Fig. 6). When the crystal is rotated 90° so that the light passes through parallel to the optic axis (path of 6 mm.) these lines disappear almost completely and instead five different lines appear between 3510A and 3630A (Table 8, Fig. 5). This occurs even at room temperature but the lines are sharper at low temperatures.

TABLE 4

ABSORPTION OF MIXED $\text{EuCl}_2\text{-BaCl}_2\text{-SrCl}_2$ CRYSTALS AT 20°K .

5% BaCl_2			10% BaCl_2		
λ	ν	Int.	λ	ν	Int.
4068.5(?)A	24,572 cm^{-1} (?)	1			
4012.7	24,913	2			
3998.2	25,003	2			
3984.7	25,088	2			
3974.0	25,156	4	3968.0A	25,194 cm^{-1}	1
3953.3	25,288	4	3949.4	25,313	1
3936.9	25,393	4	3931.2	25,430	1
3919.9	25,503	4	3917.4	25,520	1
3902.4	25,618	3	3898.9	25,641	1
3886.7	25,722	2			
3872.2	25,817	2			
3837.1	26,053	3	3830.5	26,099	1
3821.0	26,164	3	3815.2	26,203	1
3805.9	26,267	3	3799.6	26,311	1
3789.9	26,378	3	3784.6	26,415	1
3775.8	26,477	3	3770.3	26,515	1
3761.7	26,576	2	3754.7	26,626	1
3745.6	26,690	2	3741.0	26,723	1
3732.0	26,787	3	3725.6	26,833	1
3717.8	26,890	2			
3703.0	26,997	3	3696.0	27,048	1
3687.9	27,108	2	3681.9	27,152	1
3672.8	27,219	2	3667.5	27,258	1
3660.9	27,307	2	3654.9	27,352	1
3644.3	27,433	2	3638.5	27,476	1
3632.0	27,525	2			
			3578.2	27,939	1

TABLE 5

LINE FLUORESCENCE OF $\text{EuCl}_2\text{-SrCl}_2$ CRYSTALS IN VIOLET

20°K .			85°K .		
λ	ν	Int.	λ	ν	Int.
4130.7A	24,202 cm^{-1}	2			
4115.7	24,290	2			
4097.7	24,396	4			
4079.9	24,503	4	4078.3A	24,513 cm^{-1}	1
4061.9	24,612	6	4059.8	24,624	3
4046.7	24,704	5	4042.7	24,729	2
4028.3	24,817	10	4024.9	24,838	4
4013.2	24,910	6	4008.5	24,940	1d*
4007.1	24,948	1			
3994.5	25,027	8	3990.8	25,050	4

*Diffuse.

TABLE 6

INFRA-RED, RED, AND ULTRAVIOLET FLUORESCENCE
OF $\text{EuCl}_2\text{-SrCl}_2$ CRYSTALS AT 85°K.

λ	ν	Int.	λ	ν	Int.
8255.4A	$12,109\text{cm}^{-1}$	1	7136.8A	$14,008\text{cm}^{-1}$	2
8237.1	12,137	1	7111.5	14,058	3
8222.6	12,158	2	7098.8	14,083	4
8207.9	12,180	1	7070.8	14,138	3d
8180.5	12,221	1	7004.9	14,272	10
8121.7	12,309	2	6971.9	14,339	4
8090.9	12,356	2	6957.4	14,369	6
8058.7	12,405	2	6935.6	14,414	4d
7758.0	12,886	1d	6910.0	14,468	3
7723.3	12,944	2d	6896.8	14,495	3
7691.2	12,998	3d	6868.0	14,556	5
7642.2	13,081		6830.5	14,636	5
7625.5	13,109	3	6783.0	14,738	3
7604.8	13,146	1d	6763.0	14,782	1
7408.7	13,494	3d	6734.2	14,845	5
7390.0	13,528	4d			
7349.1	13,603	5d	3165.3	31,584	1
7307.9	13,680	4d	3158.7	31,650	1
7289.8	13,714	5	3151.2	31,725	2
7279.6	13,733	4	3144.3	31,794	2
7242.6	13,803	3	3138.4	31,854	1
7195.0	13,895	4	3130.9	31,930	1
7173.8	13,936	2			

TABLE 7

ABSORPTION OF Eu^{++} IN $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ AT 85°K.
LIGHT PERPENDICULAR TO OPTIC AXIS

λ	ν	Int.	λ	ν	Int.
3252.7A	$30,735\text{cm}^{-1}$	1d	3195.5A	$31,285\text{cm}^{-1}$	6D [†]
3244.6	30,812	3	3193.0	31,310	3
3231.5	30,937	4	3188.1	31,358	4
3228.0	30,968	4w*	3182.2	31,416	10
3224.7	31,002	1d	3176.4	31,473	5d
3218.9	31,058	2d	3173.6	31,501	9
3214.4	31,101	1d	3168.8	31,549	3d
3209.4	31,150	2d	3165.2	31,584	9
3204.1	31,201	4d	3163.7	31,600	9
3198.2	31,259	8			

*Wide.

†Double line.

TABLE 8

ABSORPTION OF Eu^{++} IN $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$
LIGHT PARALLEL TO OPTIC AXIS

85°K.			300°K.		
λ	ν	Int.	λ	ν	Int.
3623.7A	27,588 cm^{-1}	8	3622.3A	27,599 cm^{-1}	8
3573.4	27,977	3	3573.3	27,978	2
3569.4	28,008	4	3568.2	28,018	4
3568.2	28,018	4			
3517.0	28,425	3	3515.5	28,437	3

Mixed crystals of $\text{Sr}(\text{NO}_3)_2$ and $\text{Eu}(\text{NO}_3)_2$ show no fluorescence and no sharp absorption even at 20°K. The continuous ultraviolet absorption extends into the visible up to about 4500A so that these crystals have a bright yellow appearance. There is a weak and very broad maximum in the absorption at 3700A. The absorption of the nitrate ion, of course, interferes below about 3200A.

The results obtained with the mixed fluoride crystals are somewhat ambiguous because chemical analysis showed that most of the europium in these crystals was present in the trivalent state. Therefore the spectra were composed of a mixture of bivalent and trivalent europium spectra. Certain aspects of the spectra can, however, be definitely assigned to one or the other of two valence states. For all of the fluoride crystals (europium in CaF_2 , SrF_2 , or BaF_2) an ultraviolet absorption continuum and a violet blue fluorescence band were observed. These, no doubt, belong to the bivalent Eu^{++} ion. Then there are many absorption and fluorescence lines which can be identified with known lines of trivalent europium. For example, Narayanchandra Chatterjee⁶ has investigated the visible parts of the absorption and fluorescence spectra of CaF_2 crystals containing 1% EuF_3 . Most of the values he obtained are very close to the values shown in Tables 9 and 10. Since Chatterjee also observed a blue fluorescence band, part of his europium must have been in the bivalent state. Nevertheless, most of his lines can be identified with corresponding lines of

⁶Narayanchandra Chatterjee, *Zeit. f. Physik*, **113**, 96 (1939).

TABLE 9

FLUORESCENCE OF Eu-CaF_2 CRYSTALS AT 300°K .

λ	ν	Int.	λ	ν	Int.
6405.2A	$15,607\text{cm}^{-1}$	2	6061.9A	$16,492\text{cm}^{-1}$	2
6381.2	15,666	2	5960.6	16,772	1
6337.9	15,773	1	5918.1	16,892	1
6322.7	15,811	1d	5814.8	17,192	1
6308.9	15,846	10	5809.4	17,208	4
6265.4	15,956	4	5763.1	17,347	3
6166.0	16,213	10	5735.6	17,429	9
6102.5	16,382	2	5284.0	18,919	2
6086.7	16,424	4			

well known europic salts. Likewise many lines of the mixed europium- SrF_2 and BaF_2 crystals reported here (Tables 11, 12, 13, and 14) correspond with known europic lines. The remaining lines may possibly originate from bivalent europium, although this seems unlikely.

An interesting phenomenon is observed in the fluorescence of the mixed fluoride crystals. The fluorescence spectrum (at room temperature or at 85°K .) of the mixed Eu-CaF_2 crystals is quite similar to that of the Eu-SrF_2 crystals. But in contrast to the fluorescence spectrum of most other europic salts, the lines in the orange part of the spectrum near $5900\text{\AA}$ are very weak and the yellow line (identified with the transition from $J = 0$ to $J = 0$) is very intense. The Eu-BaF_2 crystals at room temperature show the normal fluorescence: intense orange lines and a very weak yellow ($0 \rightarrow 0$) line. At 85°K ., however, these intensities are reversed and the spectrum is very similar to the Eu-CaF_2 and Eu-SrF_2 fluorescence spectra.

The radius of the Pb^{++} ion is practically equal to that of the Eu^{++} ion and most lead salts are isomorphous with the corresponding europous salts. Therefore an attempt was made to prepare mixed crystals of PbCl_2 and EuCl_2 so that their spectrum could be studied. The attempt failed because of the strong reducing properties of bivalent europium; the lead was reduced to the metallic state.

TABLE 10
ABSORPTION OF Eu-CaF₂ CRYSTALS

85°K.			300°K.		
λ	ν	Int.	λ	ν	Int.
5761.8A	17,351cm ⁻¹	2			
5733.5	17,436	7	5732.2A	17,440cm ⁻¹	4
			5293.4	18,886	2
5284.4	18,918	2	5284.2	18,918	10
5250.8	19,038	1	5249.5	19,043	2
5224.6	19,134	2	5224.9	19,133	2
			4799.5	20,829	1
			4780.5	20,912	1
4678.0	21,370	1	4678.6	21,367	3
4662.3	21,442	1	4660.9	21,448	1
4652.0	21,489	2			
4649.3	21,502	3	4647.9	21,508	3D
4631.8	21,583	4	4630.9	21,587	4
4629.2	21,596	3	4628.2	21,600	3
4623.2	21,623	2			
4620.1	21,638	1			
4614.6	21,664	2			
4611.5	21,678	1			
4604.5	21,711	1			
4601.1	21,727	10	4600.8	21,728	10
			4205.2	23,772	1
4131.5	24,197	2	4130.9	24,201	9
			4113.4	24,304	2
4095.0	24,413	1			
4074.4	24,536	1			
4031.7	24,796	2			
4030.2	24,805	2	4029.4	24,811	3D
4018.2	24,879	5	4016.6	24,890	5
4008.7	24,938	3			
4007.1	24,948	2	4007.2	24,947	3D
3937.9	25,386	1			
3911.9	25,555	3D	3912.3	25,553	3
3894.4	25,670	3	3894.7	25,668	2
3831.2	26,093	2			
3822.3	26,154	2	3821.6	26,160	2
3801.6	26,297	1			
3797.2	26,326	6	3796.7	26,331	4
3774.1	26,488	4	3775.7	26,478	2
			3642.1	27,448	2
3612.7	27,672	3			
3608.8	27,702	5	3609.0	27,700	4
3600.6	27,765	3	3601.5	27,758	2

TABLE 11
FLUORESCENCE OF Eu-SrF₂ CRYSTALS

85°K.			300°K.		
λ	ν	Int.	λ	ν	Int.
6506.3A	15,365cm ⁻¹	1	7410.6A	13,490cm ⁻¹	6
			7081.0	14,118	3
			7056.0	14,168	4
			7026.9	14,227	6
			7009.1	14,263	4
			6942.0	14,401	3
			6687.5	14,949	1
			6616.2	15,110	1
			6595.8	15,157	1
			6572.8	15,210	3
			6556.0	15,249	1
			6545.4	15,273	1
			6510.0	15,356	2
			6465.8	15,461	1
6404.0	15,610	2	6447.5	15,505	1
6370.8	15,692	6	6402.4	15,615	4
6303.6	15,859	7	6370.3	15,693	6
6291.4	15,890	9	6291.3	15,890	10
6248.6	15,999	3	6249.5	15,996	6
6223.0	16,065	1	6220.6	16,071	4
6184.4	16,165	10	6181.3	16,173	10
6110.3	16,361	1	6131.0	16,306	3
6095.9	16,400	2	6111.2	16,359	5
6088.9	16,418	2	6091.9	16,410	6
6066.3	16,480	2	6065.5	16,481	4
6034.1	16,567	1	6033.1	16,570	1
			5985.7	16,701	1
			5943.6	16,820	1
5911.8	16,910	2	5910.2	16,915	4
5895.0	16,959	1	5893.7	16,962	4
			5858.3	17,065	0
			5812.2	17,200	3
5798.5	17,240	7	5796.5	17,247	6
			5768.8	17,329	2
5760.4	17,355	2	5757.8	17,363	6
			5744.3	17,403	2
5726.3	17,458	9	5723.0	17,468	10
			5664.9	17,647	3
			5629.6	17,758	2
			5498.1	18,183	0
			5430.6	18,409	0
5276.0	18,948	7	5274.4	18,954	5
			5247.4	19,051	0
			5234.7	19,096	0
			5225.2	19,132	0
			5214.9	19,170	0

TABLE 12
ABSORPTION OF Eu-SrF₂ CRYSTALS

85°K.			300°K.		
λ	ν	Int.	λ	ν	Int.
5756.7A	17,366cm ⁻¹	2	5753.3A	17,376cm ⁻¹	1
5721.2	17,474	6	5722.7	17,469	7
			5290.6	18,896	1
5275.2	18,951	3	5274.4	18,954	8
5248.0	19,049	1			
5217.4	19,161	1			
4667.1	21,420	1	4666.6	21,422	1
4652.2	21,489	2			
4645.0	21,522	3			
4642.3	21,535	4	4641.8	21,536	2
4625.2	21,614	5	4623.9	21,620	3
4621.0	21,634	5	4620.1	21,638	3
4606.5	21,702	2			
4592.3	21,765	10	4591.5	21,773	10
4554.0	21,952	1			
4529.8	22,069	1			
4122.7	24,249	3	4121.4	24,257	9
			4104.9	24,354	1
4086.4	24,464	3	4084.6	24,475	1
4018.7	24,876	3D	4016.8	24,888	2
4008.7	24,938	1			
4005.3	24,959	4			
4004.5	24,965	4	4003.6	24,970	3
3994.2	25,029	2	3993.2	25,035	1
3923.0	25,483	1			
3913.3	25,546	1			
3891.5	25,689	1			
3825.9	26,130	1			
3823.7	26,145	1			
3814.0	26,211	2	3814.5	26,208	1
3791.0	26,371	5	3790.6	26,373	3
3771.0	26,510	3	3771.7	26,506	2
3743.5	26,705	1			
3621.6	27,604	1			
3607.6	27,712	6			
3595.7	27,803	1			

TABLE 13
FLUORESCENCE OF Eu-BaF₂ CRYSTALS

85°K.			300°K.		
λ	ν	Int.	λ	ν	Int.
			6989.3A	14,303cm ⁻¹	4d
			6889.5	14,510	2d
			6512.4	15,350	2d
			6505.1	15,368	2d
			6485.8	15,413	2d
			6474.1	15,442	1
6395.7A	15,630cm ⁻¹	2			
6367.4	15,700	4			
			6318.1	15,823	1
6273.5	15,936	9			
6257.5	15,976	3	6261.2	15,967	5d
6240.8	16,019	2	6240.6	16,019	5d
6233.8	16,037	2			
			6212.9	16,091	3d
			6198.2	16,129	8d
6189.6	16,151	10	6184.2	16,165	8d
			6164.5	16,217	3d
			6138.4	16,286	10d
6130.8	16,306	2	6129.9	16,308	10d
			6092.3	16,409	1d
6048.1	16,529	2			
			5991.8	16,685	2d
			5971.5	16,741	3d
			5945.6	16,814	3d
			5924.2	16,875	3d
5912.0	16,910	2	5909.5	16,916	10d
5901.1	16,941	2			
5894.0	16,961	2	5891.0	16,970	10d
5859.0	17,063	2	5860.1	17,060	10d
5802.8	17,228	3			
			5790.7	17,264	1
			5761.7	17,351	3d
			5747.9	17,393	3d
			5735.0	17,432	1
5727.8	17,454	9	5727.9	17,453	1
			5627.1	17,766	1
			5495.7	18,190	2
5277.7	18,941	2			
			5243.3	19,066	1
			5098.7	19,606	1
			4690.5	21,313	2
			4637.0	21,558	1
			4556.6	21,939	1

TABLE 14
ABSORPTION OF Eu-BaF_2 CRYSTALS

85°K.			300°K.		
λ	ν	Int.	λ	ν	Int.
5763.3A	17,346 cm^{-1}	4	5763.7A	17,345 cm^{-1}	1
5728.1	17,453	6	5725.8	17,460	5
			5364.1	18,637	5
			5277.4	18,943	5
5269.0	18,973	3	5266.0	18,984	2
5254.1	19,027	3	5250.8	19,038	2
5246.7	19,054	9	5243.3	19,066	6
4674.2	21,388	9	4674.8	21,384	7
4653.8	21,481	10	4654.1	21,480	10
4642.5	21,534	2	4644.1	21,525	1
4634.6	21,570	2	4635.3	21,567	1
4620.8	21,634	8	4621.8	21,630	5
4611.9	21,676	2			
4599.4	21,736	3			
4595.0	21,756	10	4594.7	21,758	6
			4179.5	23,919	1
			4169.1	23,979	1
			4120.2	24,263	3
4040.7	24,741	3	4039.2	24,750	2
			4021.1	24,861	1
3988.0	25,067	1			
3956.2	25,269	1			
3945.9	25,335	4			
3935.9	25,399	3d			
3930.0	25,437	4	3930.2	25,436	6d
3925.4	25,467	10vd*	3924.5	25,473	10vd
			3756.0	26,615	3
			3611.4	27,681	2

*Very diffuse.

DISCUSSION OF RESULTS

The bivalent europium ion, Eu^{++} , is isoelectronic with the trivalent gadolinium ion, Gd^{+++} . The basic state of the Gd^{+++} ion has been well established as $4f^7 8s_{7/2}^0$. Russell, Albertson, and Davis⁷ have shown that the ground level of EuIII (Eu^{++}) in the gaseous phase is also $4f^7 8s_{7/2}^0$. Klemm and Döhl⁸ have measured the magnetic susceptibilities of various europous salts from which they calculated the magnetic moments. They report the following values which are independent of temperature: 7.45, 7.91, 7.95, and 7.87 Bohr magnetons for EuF_2 , EuCl_2 , EuBr_2 , and EuI_2 respectively. The value calculated for the Gd^{+++} ion ($g \sqrt{J(J+1)}$) is 7.94 magnetons and it is independent of temperature. The agreement is excellent except for europous fluoride. Klemm and Döhl believe that this is because some of the europium in this compound was present as the trivalent ion. This seems very likely in view of the fact that EuF_2 is very easily oxidized by the air. It thus appears that the Eu^{++} ion has the same electronic configuration in its ground state as the Gd^{+++} ion.

A similar situation exists with the bivalent samarium ion, Sm^{++} , and the trivalent europium ion, Eu^{+++} since both have the same basic state, $7F_0$. Butement and Terrey⁹ investigated the absorption spectra of these two ions in aqueous solution and found that although Sm^{++} gives diffuse bands, the maxima lie close to the lines of Eu^{+++} . They are shifted somewhat to longer wavelengths as expected from the smaller nuclear charge of Sm^{++} . In view of these facts it is reasonable to expect similar spectra from the bivalent europium and trivalent gadolinium ions.

The experiments, however, failed to reveal any similarity. The Eu^{++} ion tends to give up one of its seven 4f electrons quite

⁷H. N. Russell, W. Albertson, and D. N. Davis, Phys. Rev., **60**, 641 (1941).

⁸W. Klemm and W. Döhl, Zeits f. anorg. allgem. Chemie., **241**, 233 (1939).

⁹Butement and Terrey, Jour. Chem. Soc. of London, **1937**, 1112.

readily, a property which is displayed in the spectrum by the intense continuous ultraviolet absorption. This may result from a transition to the conduction band (or bands) of the crystal lattice. Experiments on the photo-conductivity of these crystals would be very useful in establishing this point. When the electron is raised to the conduction band it leaves a positive hole behind and it moves in the lattice until it is trapped at a lattice defect where it remains until released (e.g., by thermal oscillations). It eventually finds another positive hole and gives up its energy either as radiation or as heat. The blue fluorescence band of the Eu^{++} ion in the anhydrous chloride and fluoride crystals probably comes from the energy released by an electron returning into a positive hole. This explanation is supported by the fact that this diffuse blue fluorescence band is substantially weaker at 20°K . where the chance of a trapped electron being released from a lattice defect is much smaller.

As reported in the last section (Tables 1 and 2), mixed $\text{EuCl}_2\text{-SrCl}_2$ crystals at low temperatures show absorption lines and diffuse bands which are superimposed upon the ultraviolet continuum. It seems very probable that these lines and diffuse bands are not independent. First, the bands are found only in the regions where lines are also found. Second, the lines are sharpest (about 1Å wide) at the minima of the diffuse absorption; they are broadest (about 5Å wide) at the maxima of the diffuse bands. Finally, the diffuse bands shift their position by the same amount as the lines when part of the SrCl_2 is replaced by BaCl_2 . It was pointed out above that a roughly constant frequency interval of $100\text{-}110\text{cm}^{-1}$ recurred very frequently among these ultraviolet absorption lines and among the violet fluorescence lines (Tables 2, 3, and 5). An adequate interpretation of these phenomena is difficult. Certain aspects of this spectrum show a striking resemblance to the spectrum of a diatomic molecule undergoing autoionization (neglecting rotational structure). In this case the electronic energy levels are those of the Eu^{++} ion and the vibrational levels may be those of the crystal lattice. It is probable that in the upper electronic states of the Eu^{++} ion in these $\text{EuCl}_2\text{-SrCl}_2$ crystals one of the original seven 4f electrons is in a perturbed outer shell, for example, 5d, 6s, and so forth. Ce^{+++} ion in some crystals shows diffuse absorption bands¹⁰

¹⁰S. Freed, Phys. Rev., 38, 2122 (1931).

in the ultraviolet which must be ascribed to transitions of the single 4f electron to outer electronic states.

At 20°K. essentially all of the transitions must originate from the lowest vibrational level of the ground electronic state. At 85°K. the population of the next higher vibrational level (about 110cm^{-1} above lowest) should be appreciable and some additional weak absorption lines should appear, shifted to the red, which correspond to transitions from this level. Most of these lines should overlap the lines coming from the transitions originating on the lowest level. However, even the remaining lines were not observed--probably because they were too weak. The absorption lines which appear at roughly equal intervals probably come from transitions to succeeding vibrational levels superimposed upon the excited electronic states. The violet fluorescence lines, then, arise from transitions to the vibrational levels of the ground state from the lowest level of an excited electronic state. In molecules different series of vibrational levels are associated with the different electronic states. But in the case of these mixed $\text{EuCl}_2\text{-SrCl}_2$ crystals, the vibrational levels of the lattice are affected only slightly by the electronic state of the Eu^{++} ions.¹¹

Even at the temperature of liquid hydrogen many of the lines from the $\text{EuCl}_2\text{-SrCl}_2$ crystals are slightly broadened (2-3Å wide). This may be caused, at least in part, by the interaction of the discrete series of levels with the continuum of levels of equal energy. Raising the temperature of these crystals has two major effects. First, the fluctuations of the electric fields about the Eu^{++} ions increase because of the greater motion of the surrounding ions. The transitions in all the individual Eu^{++} ions are not exactly identical because the energy levels fluctuate with the fields. The integrated effect is increased broadening of the lines. Second, the higher vibrational levels of the lowest electronic state become populated. Many new transitions become possible and these overlap those which originate in the lowest vibrational level. The result is that the lines become blurred over into diffuse bands. At room temperature even the diffuse bands are almost gone and only the continuum of absorption remains throughout the ultraviolet.

¹¹The measurements are accurate to about 5cm^{-1} but the frequency intervals often vary by more than this amount.

One experiment was performed to determine whether mechanical strains in the crystals had any effect on the spectrum (e.g., on the vibrational frequencies). Some of the $\text{EuCl}_2\text{-SrCl}_2$ crystals were heated in a vacuum almost to the melting point and then annealed very carefully. Their spectrum was identical with that of the unannealed crystals. In other experiments the amount of europium in these crystals ($\text{EuCl}_2\text{-SrCl}_2$) was varied from a few mole per cent to less than 0.01 mole per cent. No shift could be detected in any of the lines or bands. The intensity, of course, decreased with decreasing europium concentration.

The great sensitivity of the bivalent europium spectrum to the symmetry of the electric fields about the Eu^{++} ion is demonstrated by the hydrated trigonal strontium chloride crystals which contained 1% Eu^{++} . The symmetry of the field is different in different crystallographic directions. Therefore an entirely different spectrum appears for each direction (perpendicular to and parallel to the optic axis). Thus far, no two crystal lattices have been found in which the bivalent europium ion has equivalent or even similar discrete spectra. This is a unique phenomenon among the rare earths. (In the case of the $\text{EuCl}_2\text{-BaCl}_2\text{-SrCl}_2$ crystals the lattice is practically identical with that of the $\text{EuCl}_2\text{-SrCl}_2$ crystals.)

The fluorescence spectrum of the trivalent europium ion is also somewhat sensitive to the electric fields. Thus the radical change in the intensity of several fluorescence lines of Eu^{+++} in BaF_2 crystals as the temperature is lowered (Table 13) must be caused merely by a change in the intensity of the electric fields around the Eu^{+++} ions brought about by a contraction of the lattice. Instead of only a single yellow line each of the Eu-alkaline earth fluoride crystals shows two yellow lines, one always weaker than the other. Since the yellow line corresponds to a $J = 0 \rightarrow J = 0$ transition,¹² only one component is possible for a field of any symmetry unless one of the following conditions is satisfied. The weaker component may be associated with a lattice vibration, the Eu^{+++} ions may occupy two different lattice positions in the crystals, or two different compounds might be present.

¹²H. Gobrecht, Ann. Physik, 28, 670 (1937); S. Freed and S. I. Weisman, J. Chem. Phys., 8, 878 (1940).

SUMMARY

The absorption and fluorescence spectra of the bivalent europium ion in various mixed crystals have been examined. A very intense continuous ultraviolet absorption is characteristic of the Eu^{++} ion. Some of the crystals show sharp absorption lines superimposed upon the continuum. At the temperature of liquid air a dilute solid solution of EuCl_2 in SrCl_2 showed over sixty absorption lines between 4000Å and 2900Å. Most of these were spaced at intervals of about $100\text{-}110\text{cm}^{-1}$. In addition, several diffuse absorption bands were present superimposed upon these lines. It was suggested that this spectrum represents autoionization of the Eu^{++} ion. There is an interaction between discrete levels of excitation and dense outer levels which may represent ionization in the lattice. The equally spaced lines are probably associated with vibrational levels of the crystal lattice which are superimposed upon the electronic states of the Eu^{++} ion. In fluorescence, these $\text{EuCl}_2\text{-SrCl}_2$ crystals at room temperature displayed an intense violet-blue band and an extreme red band. At low temperatures several fluorescence lines spaced at $100\text{-}110\text{cm}^{-1}$ intervals were superimposed upon the violet band and about forty fluorescence lines appeared in the extreme red and near infra-red.

The corresponding hydrated trigonal crystals showed no fluorescence. When light passed through perpendicular to their optic axis a group of about twenty absorption lines was obtained near 3200Å. These lines disappeared when light traversed the crystal parallel to its optic axis but five different lines appeared between 3510Å and 3630Å. Mixed crystals of $\text{Eu}(\text{NO}_3)_2$ and $\text{Sr}(\text{NO}_3)_2$ are yellow and do not fluoresce. They show no sharp absorption even at 20°K . but they do have a very weak broad absorption maximum at 3700Å. Crystals of europium fluoride in each of the alkaline earth fluorides (CaF_2 , SrF_2 , BaF_2) were prepared but most of the europium was found to be in the trivalent state. They displayed a violet-blue fluorescence band and a continuous ultraviolet absorption which were ascribed to bivalent europium. In addition many sharp absorption and fluorescence lines were obtained

but apparently most of these (if not all) originated in the trivalent europium. Several fluorescence lines of the Eu-BaF_2 crystals showed striking changes in their intensity when the crystals were cooled from room temperature to 85°K .

